Journal of Hazardous Materials 170 (2009) 1236–1241

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

The feasibility of enhanced soil washing of *p*-nitrochlorobenzene (pNCB) with SDBS/Tween80 mixed surfactants

Huiqin Guo, Zhenyu Liu, Shaogui Yang, Cheng Sun*

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Hankou Road, No. 22, Nanjing 210093, PR China

ARTICLE INFO

Article history:
Received 5 April 2009
Received in revised form 20 May 2009
Accepted 22 May 2009
Available online 28 May 2009

Keywords:
pNCB
SDBS/Tween80
Soil remediation
Water solubility
Apparent soil–water distribution constant
Desorption ratio

ABSTRACT

The present study investigated the feasibility of using two mixed surfactants, anionic surfactant sodium dodecylbenzenesulfonate (SDBS) and nonionic surfactant polysorbate 80 (Tween80), for the remediation of p-nitrochlorobenzene (pNCB) contaminated soil. The water solubility, the apparent soil–water distribution constant (K_d^*) and the desorption ratio of pNCB, as well as the sorption of surfactants by the soil were significantly affected by the dosage of surfactants and the mass ratio of SDBS/Tween80. Because of the formation of mixed micelles, the presence of SDBS showed more effective than individual Tween80 for increasing the water solubility, decreasing the K_d^* and enhancing the desorption ratio of pNCB, as well as inhibiting the sorption of surfactants by the soil. Low dosage of surfactants (Tween80 < 2000 mg L^{-1}) increased the K_d^* value and inhibited the desorption of pNCB from soil. However, relative high concentration of Tween80 had positive effect on the decrease of the K_d^* value and increase of pNCB desorption. In addition, among the tested surfactant systems, mixed SDBS/Tween80 with a 1:1 mass ratio exhibited the highest pNCB desorption. The results indicated that it is feasible to use mixed SDBS/Tween80 surfactants for the remediation of pNCB contaminated soil.

1. Introduction

Contamination of soils by toxic compounds, especially by the persistent organic pollutants has become an issue of worldwide concern. Soil is a complex matrix permanently interacting with other environmental compartments such as waters and air, thus its pollution can directly propagate contamination to surface, groundwater and air. New soil remediation technologies include bioremediation, physical and chemical remediation, and their combination technologies, which mainly emphasize the transformation and detoxification of pollutants in soil [1,2]. Bioremediation enables permanent elimination of pollutants by in situ remediation at low cost. However, for toxic persistent organic pollutants, bioremediation is limited by the correct selection of active microbes, the appropriate soil conditions for microbial activity, recalcitrance of pollutants to biodegradation, and formation of metabolites which may be more toxic than the parent contaminant. Among the physical and chemical remediation techniques, soil washing is a valid and relatively inexpensive alternative in soil remediation [3]. It is based on the fact that desorption of pollutants from contaminated soils into liquid phases which are then disposed or subjected to further chemical or biochemical treatments for complete detoxification [4].

Surfactant enhanced remediation (SER) has been proposed as a promising technique for the in situ remediation of contaminated soils and/or groundwater in recent years [5–9]. In principle, the addition of certain concentration of surfactants favors the formation of micelles and enhances the solubility of organic compounds, which is very helpful for increasing the mass transfer of hydrophobic compounds (HOCs) from soil surface to aqueous phase, further improving the contact probability of HOCs with microorganism for possible biodegradation [10,11]. Compared with using single surfactant, previous studies have shown that using anionic–nonionic mixed surfactants was more effective for the solubility enhancement and desorption of HOCs from soils. This is because the mixed anionic–nonionic surfactants generally show smaller critical micelle concentrations (CMCs), higher cloud point and lower Krafft point [12,13]. In addition, the addition of nonionic surfactants to anionic surfactant solution could decrease the precipitation between anionic surfactant and multivalent electrolyte such as Ca^{2+} and Mg^{2+}, which correspondingly decrease the adsorption loss of the anionic surfactant by soils [6,11,14]. Therefore, the mixed surfactants use in the remediation of contaminated soils or groundwater has attracted more attention in recent years, which can be applied in a wide range of subsurface conditions (e.g., temperature, salinity and hardness) compared with single surfactant.

p-Nitrochlorobenzene (pNCB) is an important chemical intermediate for organic synthesis, including *p*-nitrophenol, azo and sulfate dyes, pharmaceuticals (such as phenacetin and acetaminophen) and pesticides (such as nitrofen and parathion)

* Corresponding author. Tel.: +86 2583593239; fax: +86 2583593239.
E-mail address: envidean@nju.edu.cn (C. Sun).

0304-3894/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2009.05.101

and rubber chemicals, etc. Meanwhile, pNCB is also listed in the Environmental Priority Pollutants by US EPA and China SEPA because of its high toxicity, non-biodegradability, bioaccumulation and biomagnify, chemical stability and serious environmental risks. The wastewater and waste gas discharged from the manufactures of organic synthesis, paints, coatings and dyes, as well as the pharmaceutical plants are the main pollution sources of the pNCB in environment. Besides, accidental spills and container rupture during storage and transportation are also important sources of the point contamination of pNCB. Due to its low aqueous solubility and vapor pressure, pNCB is easily adsorbed by the soil particles during their transportation in various environmental media which results in a large storage of pNCBs in soil. However, little information is available for the remediation of pNCBs contaminated soil, and to the best of our knowledge, there is no report in literature of using the mixed surfactants for the desorption of pNCB from soil particles.

Therefore, the aim of the present study is to evaluate the feasibility of using mixed two different kinds of surfactants, i.e. anionic surfactant sodium dodecylbenzenesulfonate (SDBS) and nonionic surfactant Polysorbate 80 (Tween80), for the remediation of pNCBs contaminated soil. The water solubility of pNCB, the distribution of pNCB in soil–water system and the desorption of pNCB from contaminated soil, as well as the sorption of Tween80 surfactant by the soil particles affected by the mixed SDBS/Tween80 surfactants were comprehensively investigated.

2. Experimental

2.1. Materials

pNCB was obtained from Shanghai Jingchun Reagents Co., Ltd. (Shanghai, China). Tween80 ($C_{64}H_{124}O_{26}$) was obtained from Nanjing Zhuyan Biotechnology Co., Ltd. (Nanjing, China). SDBS ($C_{12}H_{25}C_6H_4SO_3^-Na^+$) was obtained from Chengdu Kelong Chemical Reagents Plant (Chengdu, China). All of the chemicals used were analytical or reagent grade, and directly used without any further purification. Deionized water was used throughout this study. Mixed surfactant solutions were prepared by dissolving Tween80 and SDBS in deionized water in terms of different mass ratios.

2.2. Experimental procedures

2.2.1. Preparation of pNCB contaminated soil

Uncontaminated natural soil was collected from Nanjing, China. The collected soil was air dried and then passed through a 0.95 mm sieve. The physical and chemical properties of the tested soil are shown in Table 1. The preparation of pNCB contaminated soil sample was followed in the methods in previous study [15]. For the amendment of contaminated soil, pNCB solution (100 mL of 2800 mg L^{-1} solution in acetone) was prepared. The solution was added to amount of 1400 g soil at five times, and each time was stirred vigorously for about 30 min to promote homogeneous distribution of pNCB in soil phase. The acetone was evaporated by leaving the samples resting for 5 days at room temperature (22 ± 2 °C) inside a hood, and then dry contaminated soil was obtained. Finally, the prepared soil samples were transferred into brown bottle and tumbled for about 1 week before desorption experiments. The resulting freshly amended soil with final concentrations of 152 mg kg^{-1} pNCB.

Table 1
Physical and chemical properties of the soil used in present study.

Parameters	Value
pH	7.23
Organic matter (OM)	1.02%
Cation exchange capacity (CEC)	18.87
Clay content (d < 0.2 mm)	37.6%

2.2.2. Water solubility of pNCB in the presence of mixed surfactants

The solubility of pNCB in aqueous solution affected by the mixed surfactants was conducted in 22 mL Corex centrifuge tubes with Teflon-lined screw caps. pNCB saturated solutions were obtained according to the following procedures. Slight excess amount of pNCB was added into a series of tubes, in which 20 mL aqueous solutions with known concentration of surfactants were added. Subsequently, the tubes were equilibrated on an end-over-end shaker for 24 h at room temperature (22 ± 2 °C) to ensure the solubility of pNCB reach the equilibrium. Finally, the samples were centrifuged at 3500 rpm for 30 min to separate the undissolved solute, and appropriate supernatant were collected for analysis. All the tests were conducted in duplicate, and the average values were presented.

2.2.3. Distribution of pNCB in water–soil system in the presence of mixed surfactants

2.00 g of uncontaminated soil sample were added into each centrifuge tube, then added 20 mL aqueous solutions with known concentration of surfactants (the initial surfactant concentration spanned over a large range of values, and all above the nominal CMC of Tween80). All the aqueous solutions for soil tests contained 12.5 mg L^{-1} pNCB, 0.02 mol L^{-1} NaCl to keep a constant ionic strength and 0.01% (w/w) NaN_3 to inhibit microbial growth. Subsequently, these samples were equilibrated on an end-over-end shaker for 24 h at room temperature (22 ± 2 °C). Preliminary experiments showed that 24 h was enough for the sorption of pNCB and surfactants to reach equilibrium, and the sorption of the pNCB and surfactants by the tubes was negligible. Finally, the tubes were centrifuged at 3500 rpm for 30 min to completely separate the solution and solid phase, and the supernatant were collected for analysis. The pH of the suspensions before and after sorption was measured and did not show significant change.

2.2.4. Desorption of pNCB from contaminated soil sample by mixed surfactants

2.00 g of prepared pNCB contaminated soil sample was mixed with 20 mL of aqueous solutions with known concentration of surfactant solution in 22 mL centrifuge tubes. The centrifuge tubes were equilibrated on an end-over-end shaker for 24 h at room temperature (22 ± 2 °C), and then were centrifuged at 3500 rpm for 30 min to separate the solution and solid phase, finally the supernatant were collected for analysis. The residual concentrations of pNCB in soil and the adsorbed amount of surfactants by soil particles were calculated by the difference between the initial and equilibrium concentrations in aqueous phase.

2.3. Analysis methods

The concentration of pNCB and Tween80 in aqueous phase were quantified by an Agilent 1200 HPLC equipped with a diode array detector (DAD). An Agilent SB-18 column (4.6 mm × 150 mm, 5 μm) was employed for the separation. The mobile phase was a mixture of methanol/water with a flow rate of 1.0 mL min^{-1}. The methanol/water ratios (v/v), sample injection volumes and the detecting wavelengths for pNCB and Tween80 were 70:30, 5 μL, 220 nm and 90:10, 20 μL, 242 nm, respectively. The calibration was conducted daily and R^2 was greater than 0.99 in all the cases.

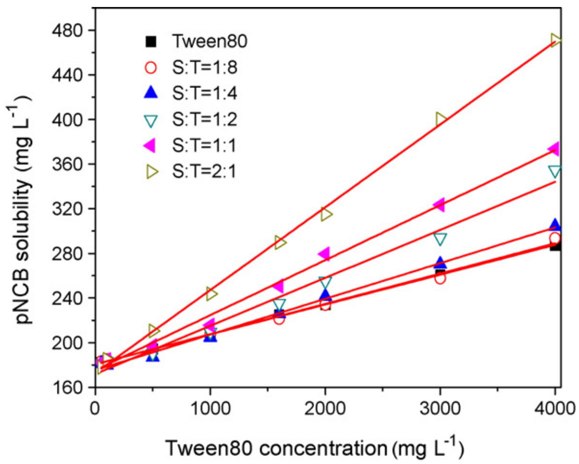

Fig. 1. Water solubility enhancement curves of pNCB in presence of the single and mixed SDBS/Tween80 surfactants.

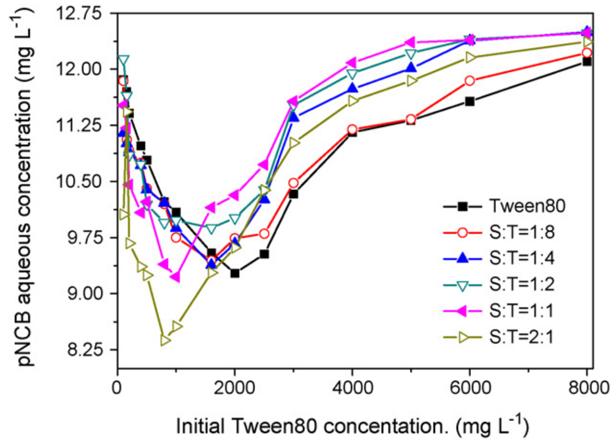

Fig. 2. The distribution of pNCB in the water–soil system in presence of single and mixed SDBS/Tween80 surfactants.

3. Results and discussion

3.1. Water solubility enhancement of pNCB by the mixed surfactants

The solubility of pNCB in aqueous solution affected by the presence of single Tween80 and mixed SDBS/Tween80 surfactants with different mass ratio were studied and the results are shown in Fig. 1. It can be seen that the total apparent solubility (S_w) of pNCB linearly increased with the increasing of Tween80 concentration. In addition, the mixed SDBS/Tween80 surfactants showed positive effect on increasing the water solubility of pNCB, and it was found that the S_w value increased with the increase of the SDBS/Tween80 ratio. Generally, the molar solubilization ratio (MSR) is used to measure the effectiveness of a particular surfactant for the solubilizing of a given solute [16]. The MSR is defined as the mole numbers of solubilized compound per mole numbers of micellized surfactant, and which is calculated as follows:

$$MSR = \frac{S_w - S_{cmc}}{C_s - CMC} \quad (1)$$

where S_{cmc} is the apparent solubility of HOCs solute in moles per litre at the CMC, S_w is the total apparent solubility of the HOCs solute in moles per litre in micellar solution at a particular surfactant concentration greater than the CMC, C_s is the surfactant concentration corresponding to a defined *s*. Based on the molar volume of water (0.01805 L mol^{-1} at 25 °C), therefore, MSR can be obtained from the slope of solubilization curves in the ranges of surfactant concentrations above CMC. The experimental regression equations of S_w *vs*. Tween80 concentration, and the MSR values of pNCB at different SDBS/Tween80 ratio are shown in Table 2. It can be observed that the MSR values of pNCB with mixed SDBS/Tween80 were higher than that with single Tween80, moreover, the MSR values were significantly increased from 0.2223 to 0.6171 with the increase of SDBS/Tween80 ratio from 0 to 2:1. This can be explained by the fact that in mixed SDBS/Tween80 surfactants, the hydrophobic tails of the SDBS can incorporate into the interior of micelles of Tween80 resulting in the formation of mixed micelles, which are usually smaller than that of the single SDBS and Tween80 [6,17]. Therefore, the decreased CMC of the mixed surfactants lead to the relative increasing of micelles concentration, which is favorable for pNCB incorporating into the surfactants micelle. The test results indicated that the solubility of pNCB in aqueous solution could be effectively enhanced by the addition of SDBS to Tween80 solution.

Table 2
pNCB solubilization enhancement by single Tween80 and SDBS/Tween80 mixed surfactants.

SDBS/Tween80	Equation of solubility enhancement	R^2	K_{mc} (L kg^{-1})	MSR
0	$Y = 0.02675X + 180.7$	0.9995	1.470×10^2	0.2223
1:8	$Y = 0.02715X + 180.5$	0.9947	1.492×10^2	0.2257
1:4	$Y = 0.03194X + 175.4$	0.9958	1.755×10^2	0.2655
1:2	$Y = 0.043X + 172.1$	0.9849	2.363×10^2	0.3574
1:1	$Y = 0.04931X + 175.3$	0.9942	2.709×10^2	0.4099
2:1	$Y = 0.07424X + 172.9$	0.9985	4.079×10^2	0.6171

3.2. Distribution of pNCB in the soil–water system in the presence of mixed surfactants

The distribution of pNCB in the soil–water system affected by the presence of single Tween80 and SDBS/Tween80 mixed surfactants at different ratio were studied and the results are shown in Fig. 2. It can be seen that when the concentration of Tween80 was below 2000 mg L^{-1}, the residual concentration of pNCB in aqueous solution sharply decreased with the increase of individual Tween80 dosage before sorption equilibrium. Subsequently, further increasing the Tween80 dosage more than 2000 mg L^{-1}, the residual concentration of pNCB in aqueous solution was correspondingly increasing. In addition, the same trends were also observed in the mixed SDBS/Tween80 surfactants. The results indicated that the presence of low dosage of Tween80 or mixed SDBS/Tween80 surfactants has a positive effect on the transfer of pNCB from water to soil particles. However, relatively high dosage of surfactants has positive effect on the opposite process.

In the surfactant-free system, the distribution of HOCs is mainly determined by the soil organic matter and it can be estimated by the soil–water distribution coefficient K_d according to partition theory [7]. With the addition of surfactant, the equilibrium distribution of pNCB between water and soil was destroyed, and in the presence of surfactant, the distribution of pNCB in soil–water system can be predicted according to the following model [18,19]:

$$K_d^* = \frac{K_d(1 + f_{sf}K_{sf}/K_d)}{1 + X_{mn}K_{mn} + X_{mc}K_{mc}} \quad (2)$$

where K_d^* is the apparent soil–water distribution coefficient for pNCB (L kg^{-1}), K_d is the sorption coefficient of pNCB by the soil particles in the absence of surfactant (L kg^{-1}), f_{sf} is the sorption amount of surfactant by the soil particles (mg kg^{-1}), K_{sf} is the distribution coefficient of pNCB with the soil-sorbed surfactant (i.e. the carbon-normalized pNCB distribution coefficient with the sorbed surfactant-derived organic carbon, L kg^{-1}), X_{mn} and X_{mc} are the

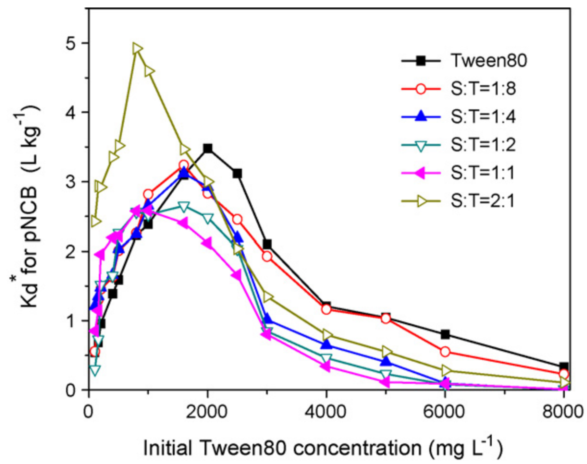

Fig. 3. The K_d^* value of pNCB affected by the single and mixed SDBS/Tween80 surfactants.

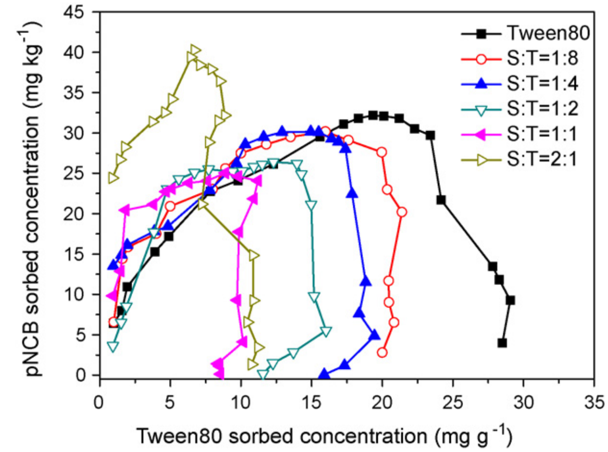

Fig. 4. The sorbed pNCB *vs*. the sorbed Tween80 surfactants in soil phase.

surfactant monomer and micellar concentrations in water, respectively (g L^{-1}), and K_{mn} and K_{mc} are the partitioning coefficients of pNCB with the surfactant monomer and micellar phases, respectively (L g^{-1}), and the K_{mc} values for different surfactant systems are shown in Table 2.

The K_d^* of pNCB as a function of the dosage of Tween80 at different SDBS/Tween80 ratios are shown in Fig. 3. It can be seen that the K_d^* of pNCB increased at first and decreased subsequently within the whole concentration of Tween80 tested from 100 to 8000 mg L^{-1}. The maximum K_d^* value of pNCB with mixed SDBS/Tween80 surfactants was lower than that with single Tween80 and appeared to be negatively related to mass fraction of SDBS in surfactant solution. For instance, the maximum K_d^* value decreased from 3.48 to 2.58 as a consequence of increasing the SDBS/Tween80 mass ratio from 0 to 1:1, which indicated that the addition of SDBS had a positive effect on the distribution of pNCB in water phase. However, when increasing the SDBS/Tween80 ratio to 2:1, the maximum K_d^* value dramatically increased to 4.92, which suggested that the presence of excess SDBS has negative effect on the distribution of pNCB in water phase.

Further, the sorbed Tween80 concentration corresponding to the points of saturated sorbed pNCB appeared to be negatively related with the mass fraction of SDBS in the mixed surfactants. For example, the sorbed Tween80 amounts decreased from 17.3 to 3.73 mg g^{-1} when the SDBS/Tween80 mass ratio increased from 0 to 2:1. According to Eq. (2), the partitioning of pNCB between soil and water (K_d^*) is enhanced by the presence of sorbed surfactants ($f_{sf}K_{sf}$) and decreased by the enhanced aqueous solubility of the pNCB in the presence of surfactant monomers ($K_{mn}X_{mn}$) and micelles ($K_{mc}X_{mc}$). In the cases of addition of appropriate of SDBS, the sorbed Tween80 is decreased (a more quantitative description of the sorption of Tween80 by soil particles at different SDBS/Tween80 ratio is given later in our discussion) and the solubilization of Tween80 for pNCB is enhanced (see Fig. 1). Both of above resulted in the decrease of K_d^*. However, it is worthy of mentioning that the effect of mixed micelle formation on the sorption of Tween80 amount is rather finite. Rao and He have reported that with the increase of total surfactant concentration in equilibrium solutions, the bilayer adsorption gradually formed through the hydrocarbon chain–chain interactions in SDBS and nonionic surfactant [20]. The above discussed contribution results in the increase of adsorbed Tween80 concentration so much as the total surfactant sorption. Although the solubilization of pNCB is always increased in the tested conditions, the larger surfactant sorption amount may play a primary role in governing the distribution of pNCB, and lead to an increase of K_d^* in the 2:1 SDBS/Tween80 system.

In order to further investigate the role of surfactants in affecting the distribution of pNCB in the soil–water system, the sorbed pNCB as a function of the sorbed Tween80 was explored and the results are shown in Fig. 4. It can be observed that the dosage of sorbed pNCB increased firstly and keep a plateau then decreased with the increase of sorbed Tween80 dosage. It can be attributed to that at low dosage of surfactants, the sorbed surfactant-derived organic carbon in the soil particles plays primary role in the pNCB adsorption, but when increasing of the dosage of surfactants, the surfactant micelles have significantly effect on the pNCB desorption from soil.

Further, it also can be seen from Fig. 4 that the maximum sorbed pNCB gradually decreased from 32.17 to 25.04 mg kg^{-1} with the increase of SDBS/Tween80 mass ratio from 0 to 1:1, but dramatically increased to 40.23 mg kg^{-1} as the SDBS/Tween80 ratio increased to 2:1. It due to the concentration of formed micelles were proportional with the fraction of SDBS. However, because of the surfactant adsorption increase in the presence of excess SDBS, further increasing the mass fraction of SDBS increased the adsorption of pNCB by the soil particles.

3.3. Desorption of pNCB from spiked soil by mixed surfactants

The desorption of pNCB from contaminated soil in the presence of single Tween80 and mixed SDBS/Tween80 surfactants at different mass ratios were studied and the results are shown in Fig. 5. It

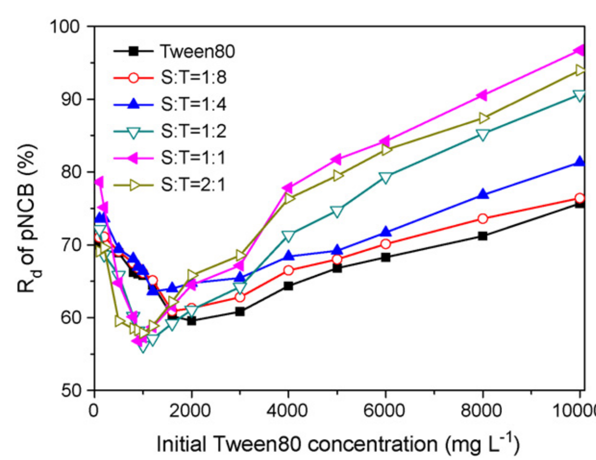

Fig. 5. The R_d of pNCB from contaminated soil by the single and mixed SDBS/Tween80 surfactants.

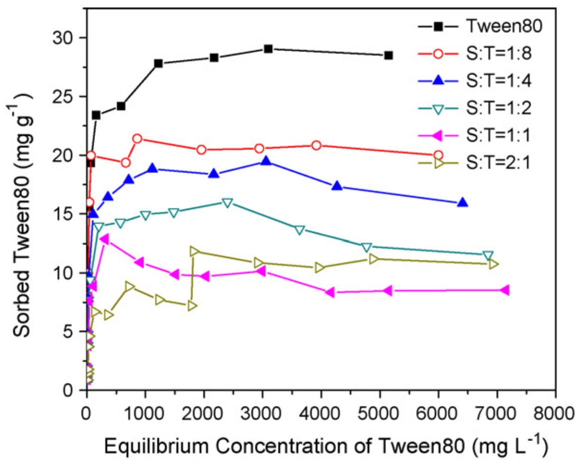

Fig. 6. Sorption isotherms of Tween80 by the soil particles.

can be seen that the desorption ratio (R_d) of pNCB as a function of Tween80 concentration showed a similar trend of "V" shaped curve in all the cases. When the concentrations of Tween80 were lower than 2000 mg L^{-1}, the R_d decreased with the increasing of addition of Tween80 dosage. For instance, R_d decreased about 15–20% in the presence of single Tween80 or mixed SDBS/Tween80 surfactants. This is due to the surfactants were adsorbed by the soil particles and resulted in the increasing of surfactant-derived organic carbon in soil phase, which lead to relative more dosage of pNCB was adsorbed by the soil particles. However, R_d increased when increasing the dosage of Tween80 from 2000 to 10,000 mg L^{-1}. This is due to the forming of more surfactant micelles plays positive role for the transfer of pNCB from soil phase to water phase. It was further observed that R_d increased with the increase of SDBS/Tween80 ratio, such as the R_d with 10,000 mg L^{-1} Tween80 increased from 75.66% to 96.71% as the SDBS/Tween80 ratio increased from 0 to 1:1. However, when further increasing the SDBS/Tween80 ratio to 2:1, the desorption ratio of pNCB did not increase more but decrease slightly.

Indeed, from Figs. 2–5, it can be observed that the mixed SDBS/Tween80 surfactants were more effective for the transfer of pNCB from soil phase to water phase than that by single Tween80, but higher SDBS/Tween80 ratio (such as 2:1) does not show better efficiency. We proposed this is because more Tween80 could be adsorbed by the soil particle in the presence of excess SDBS. In order to demonstrate our proposal, the sorption of Tween80 by soil particles at different SDBS/Tween80 ratio was explored, and the results are showed in Fig. 6. As can be seen from Fig. 6, the sorption of Tween80 dosage after equilibrium was decreased with the increase of SDBS/Tween80 ratio from 0 to 1:1, and then did not decrease but slight increased when further increased SDBS/Tween80 ratio to 2:1. The results were consistent with our previous hypothesis. For the inhibition of the sorption of Tween80 by the addition of appropriate ratio of SDBS, it can be attributed to the presence of anionic surfactant molecules SDBS increased the negative surface charge of the mixed micelle shell. As a result, the electrostatic repulsions between mixed micelles and soil became stronger, while hydrogen bonding and electrostatic attraction between Tween80 in mixed micelles and soil was inhibited [6]. In addition, the formation of mixed micelles could decrease the CMC and the monomer concentration, and which inhibited the sorption of Tween80 onto the soil particles. However, at the condition of excess SDBS, the precipitation between anionic surfactant and multivalent electrolyte such as Ca^{2+} and Mg^{2+} could be enhanced, and which potentially resulted in more surfactants (both SDBS and Tween80) were adsorbed by the soil particles [14,21–23].

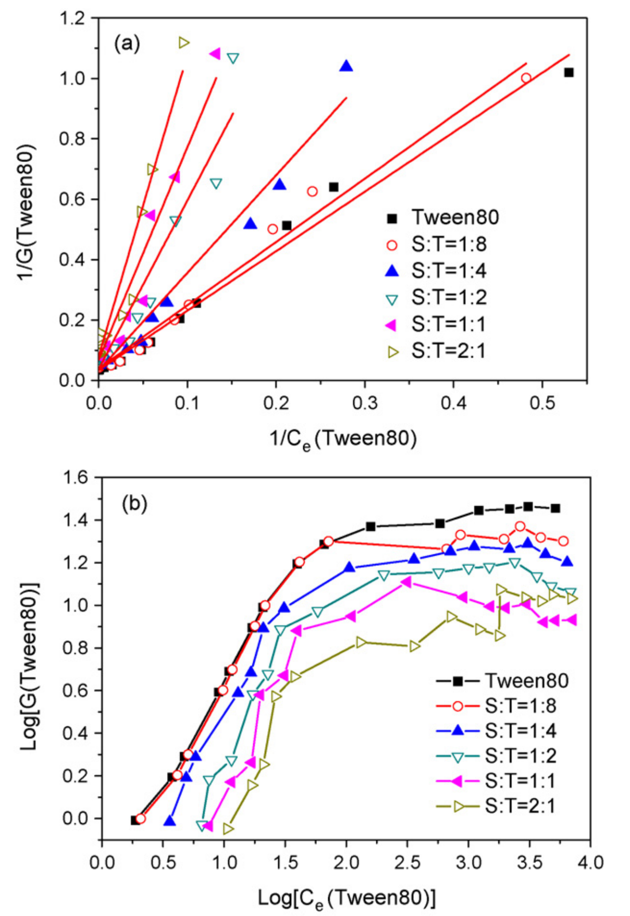

Fig. 7. Sorption isotherm models of Tween80: (a) the Langmuir model; (b) the Freundlich model.

3.4. The sorption isotherms of Tween80 surfactant by soil particles

In order to further evaluate the sorption of surfactants by the soil particles, two conventional models, the linear Langmuir isotherms model (Eq. (3)) and the Freundlich isotherms model (Eq. (4)), are used to describe the sorption of Tween80 by soil particles, and the results are shown in Fig. 7 and Table 3.

$$\frac{1}{q} = \frac{1}{q_m} + \frac{1}{Kq_m} \times \frac{1}{c} \quad (3)$$

$$\log q = \frac{1}{n}\log c + \log K \quad (4)$$

where q is the amount of adsorbed Tween80 in soil phase (mg g^{-1}), K is the adsorption constant of Tween80, q_m is the maximum amount of adsorbed Tween80 in soil phase (mg g^{-1}), $1/n$ represents the nonlinearity degree of the sorption, and c is the equilibrium concentration of Tween80 in aqueous phase (mg L^{-1}).

As can be seen from Fig. 7 and Table 3, the sorption isotherms of Tween80 can be fitted adequately with the Langmuir sorption model. It suggests that the adsorption of Tween80 is unimolecular layer form mainly in both single and mixed surfactants systems, and the adsorption reaches to a saturation as all the soil surface to be occupied. There is a decrease trend of the q_m when the SDBS/Tween80 mass ration increased from 0 to 2:1, which decreased from 29.38 to 12.58 mg g^{-1}. Consistent with the report of Yuan et al., the varying relationship similarly suggests that the sorption of Tween80 is greatly inhibited by SDBS especially in presence of higher proportions of SDBS [24]. Furthermore, the results also fitted with a one-site Freundlich sorption model, which is suitable

Table 3
Langmuir and Freundlich sorption equations of Tween80 in single and SDBS/Tween80 mixed surfactants.

SDBS/Tween80	Langmuir sorption model			Freundlich sorption model			
	Equation	q_m (mg g^{-1})	R^2	Equation	R^2	K	$1/n$
0	$Y = 1.9703X + 0.03404$	29.38	0.9853	$Y = 0.7925X - 0.1771$	0.9506	0.67	0.7925
1:8	$Y = 2.0980X + 0.03892$	25.69	0.9849	$Y = 0.9177X - 0.3059$	0.9823	0.49	0.9177
1:4	$Y = 3.2356X + 0.03258$	30.69	0.9756	$Y = 0.8382X - 0.3637$	0.9306	0.43	0.8382
1:2	$Y = 5.5894X + 0.03713$	26.93	0.9248	$Y = 1.0814X - 0.8181$	0.9284	0.15	1.0814
1:1	$Y = 7.0422X + 0.06783$	14.74	0.9394	$Y = 1.2551X - 1.1581$	0.9384	0.069	1.2551
2:1	$Y = 9.9767X + 0.07949$	12.58	0.9386	$Y = 1.3833X - 1.4969$	0.9215	0.032	1.3833

for the low concentration of surfactants but deviates for high concentration. As is well known, in the Freundlich isotherms model, the constant value of $1/n$ is the heterogeneity factor which indicates the relative distribution of energy sites and depends upon the nature and strength of the adsorption process. If the $1/n$ is lower than 1, it means the sorption occurs mainly in the surface of heterogeneous adsorbent and dense organic matter, the adsorption points with higher energy are occupied firstly by solute molecules and then the lower points; if the $1/n$ is greater than 1, it represents the surface structure of soil is altered by the adsorbed solute molecules, which enhances the further adsorption of solute. It can be observed from Table 2 that the value of $1/n$ showed an increasing trend from 0.7925 ($1/n < 1$) to 1.3833 ($1/n > 1$) as a function of increasing SDBS/Tween80 mass ratio from 0 to 2:1, which reflects that the active sites having equal energy where adsorption can take place increased from 79.25% to 138.33% [25]. It suggests that the presence of SDBS increased the adsorption active sites of Tween80 in soil particles.

4. Conclusions

(1) Because of the formation of mixed micelles, the mixed SDBS/Tween80 surfactants were more effective on the enhancement of the apparent solubilities of pNCB (S_W) and decrease of Tween80 adsorption. S_W, MSR and sorbed Tween80 concentration were positively related to the mass fraction of SDBS in mixed surfactant solutions.

(2) The distribution of pNCB in soil–water system and the desorption ratio of pNCB from contaminated soil were significantly effected by the dosage of Tween80 in individual surfactant or the mixed SDBS/Tween80 surfactants. Low dosage of Tween80 (<2000 mg L^{-1}) could increase the K_d^* value of pNCB and inhibit the desorption of pNCB from soil particles, but relative high concentration of Tween80 could effectively decrease the K_d^* value and increase the desorption ratio of pNCB.

(3) After the adsorption saturation (2000 mg L^{-1}) dosage of Tween80, the presence of SDBS showed positive effect on the decrease of the K_d^* value and enhancement of the desorption percentage of pNCB. The 1:1 mass ratio of SDBS/Tween80 system exhibited the best effect in the tested conditions. The present study indicated that it is feasible to use mixed SDBS/Tween80 surfactants for the remediation of pNCB contaminated soil.

Acknowledgements

This work was supported by the the Jiangsu Province Social Development Foundation (BS2007051), the cooperation programs of “Research of green washing technology on high concentration of organic contaminants pollution site”, State Environmental Protection Administration and Nanjing Research Institute of Environmental Protection. The authors wish to thank the Dr. Chenggang Gu and Yonghua Wang, School of the Environment, Nanjing University, for valuable writing assistance.

References

[1] P. Conte, A. Agretto, R. Spaccini, A. Piccolo, Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils, Environ. Pollut. 135 (2005) 515–522.
[2] B. Wen, R. Li, S. Zhang, X. Shan, J. Fang, K. Xiao, S.U. Khan, Immobilization of pentachlorophenol in soil using carbonaceous material amendments, Environ. Pollut. 157 (2009) 968–974.
[3] M.I. Kuhlman, T.M. Greenfield, Simplified soil washing processes for a variety of soils, J. Hazard. Mater. 66 (1999) 31–45.
[4] M.J. Mann, Full-scale and pilot-scale soil washing, J. Hazard. Mater. 66 (1999) 119–136.
[5] W.W. John, G. Bao, W.P. Johnson, T.B. Stauffer, Sorption of nonionic surfactant oligomers to sediment and PCE DNAPL: effects on PCE distribution between water and sediment, Environ. Sci. Technol. 34 (2000) 672–679.
[6] K. Yang, L. Zhu, B. Xing, Enhanced soil washing of phenanthrene by mixed solutions of TX100 and SDBS, Environ. Sci. Technol. 40 (2006) 4274–4280.
[7] C.T. Chiou, L.J. Peters, V.H. Freed, Physical concept of soil water equilibrium for non-ionic organic-compounds, Science 206 (1979) 831–832.
[8] D.E. Kile, C.T. Chiou, Water solubility enhancements of DDT and trichlorobenzene by some surfactants below and above the critical micelle concentration, Environ. Sci. Technol. 23 (1989) 832–838.
[9] J.C. Mata-Sandoval, J. Karns, A. Torrents, Influence of rhamnolipids and Triton X-100 on the desorption of pesticides from soils, Environ. Sci. Technol. 36 (2002) 4669–4675.
[10] H. Yu, L. Zhu, W. Zhou, Enhanced desorption and biodegradation of phenanthrene in soil–water systems with the presence of anionic–nonionic mixed surfactants, J. Hazard. Mater. 142 (2007) 354–361.
[11] B. Zhao, L. Zhu, W. Li, B. Chen, Solubilization and biodegradation of phenanthrene in mixed anionic–nonionic surfactant solutions, Chemosphere 58 (2005) 33–40.
[12] A.H. Saiyad, S.G. Bhat, A.K. Rakshit, Physicochemical properties of mixed surfacant systems: sodium dodecyl benzene sulfonate with triton X 100, Colloid Polym. Sci. 276 (1998) 913–919.
[13] P.L. Dubin, J.M. Principi, B.A. Smith, M.A. Fallon, Influence of ionic strength and composition on the size of mixed micelles of sodium dodecyl sulfate and Triton X-100, J. Colloid Interf. Sci. 127 (1989) 558–565.
[14] K.L. Stellner, J.F. Scamehorn, Hardness tolerance of anionic surfactant solutions. 2. Effect of added nonionic surfactant, Langmuir 5 (1989) 77–84.
[15] J.C. Mata-Sandoval, J. Karns, A. Torrents, Influence of rhamnolipids and Triton X-100 on the biodegradation of three pesticides in aqueous phase and soil slurries, J. Agric. Food Chem. 49 (2001) 3296–3303.
[16] D.A. Edwards, R.G. Luthy, Z. Liu, Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions, Environ. Sci. Technol. 25 (1991) 127–133.
[17] T. Okano, T. Tamura, Y. Abe, T. Tsuchida, S. Lee, G. Sugihara, Micellization and adsorbed film formation of a binary mixed system of anionic/nonionic surfactants, Langmuir 16 (2000) 1508–1514.
[18] L. Zhu, S. Feng, Synergistic solubilization of polycyclic aromatic hydrocarbons by mixed anionic–nonionic surfactants, Chemosphere 53 (2003) 459–467.
[19] J.G. Muller, P.T. Chapman, P.H. Pritchard, Action of a fluoranthene-utilizing bacterial community on polycyclic aromatic hydrocarbon components of creosote, Appl. Environ. Microb. 55 (1989) 3058–3090.
[20] P. Rao, M. He, Adsorption of anionic and nonionic surfactant mixtures from synthetic detergents on soils, Chemosphere 63 (2006) 1214–1221.
[21] P. Wang, A.A. Keller, Partitioning of hydrophobic pesticides within a soil–water–anionic surfactant system, Water Res. 43 (2009) 706–714.
[22] K.L. Stellner, J.F. Scamehorn, Hardness tolerance of anionic surfactant solutions. 1. Anionic surfactant with added monovalent electrolyte, Langmuir 5 (1989) 70–77.
[23] C.T. Jafvert, Sediment and saturated-soil-associated reactions involving an anionic surfactant (dodecyl sulfate). 2. Partition of PAH compounds among phases, Environ. Sci. Technol. 25 (1991) 1039–1045.
[24] S. Yuan, Z. Shu, J. Wan, X. Lu, Enhanced desorption of hexachlorobenzene from kaolin by single and mixed surfactants, J. Colloid Interf. Sci. 314 (2007) 167–175.
[25] M. Mufazzal Saeed, A. Ghaffar, Adsorption syntax of Au(III) on unloaded polyurethane foam, J. Radioanal. Nucl. Chem. 232 (1998) 171–177.